

(19) Japan Patent Office (JP)

(11) Japanese Unexamined Patent Application Publication Number

(12) Japanese Unexamined Patent Application Publication (A)

2003-238577

(P2003-238577A)

(43) Publication date: August 27, 2003

(51) Int. Cl. ⁶	Identification Symbol	Office Reference Number location	FI	Technical indication
C07F 7/18			C07F 7/18	W 2K009
C09K 3/00	112		C09K 3/00	112F 4H020
3/18	104		3/18	104 4H049
G02B 1/10			G02B 1/10	A Z
1/11				
Request for examination: Not yet requested			No. of claims: 7 OL (Total of 11 pages)	
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(32) Priority Date	October 5, 2001		(72) Inventor	
(33) Priority Country	Japan (JP)		(72) Inventor	
(31) Priority No.	Patent Application No. 2001-378382 (P2001-378382)		(74) Agent	100079304 Takashi KOJIMA (including 2 other persons)
(32) Priority Date	December 12, 2001		F term (Reference)	2K009 AA05 AA15 BB02 BB06 BB11 CC02 CC03 CC09 CC26 CC42 DD02 DD03 DD06 EE05 4H020 BA31 4H049 VN01 VP02 VQ21 VR21 VR43 VU21 VW02
(33) Priority Country	Japan (JP)			

(54) Title of the invention:

PERFLUOROPOLYETHER-MODIFIED SILANE, SURFACE TREATING AGENT, AND ANTIREFLECTION FILTER

(57) Abstract (Amended)

Solving Means: A perfluoropolyether-modified silane represented by the following general formula (1):

(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

Effects: The perfluoropolyether-modified silane in the present invention is excellent in terms of water and oil repellency, parting properties, chemical resistance, lubricity, durability, antifouling properties, and a fingerprint wiping-off property since it has no

polar group, can be used as a surface treating agent for coating on the surfaces of various substrates, and can be applied to an antireflection filter in which a cured film is formed on the surface. Further, the antireflection filter of the present invention is characterized, for example, in that it is resistant to staining and easy to wipe off such stains, and has good surface lubricity and resistance to marring, which performances are maintained over a long term.

Scope of Patent ClaimsClaim 1

A perfluoropolyether-modified silane represented by the following general formula (1):

[Chem. 1]



(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

Claim 2

The perfluoropolyether-modified silane as described in claim 1, wherein the hydrolyzable group X is an organooxy group.

Claim 3

A surface treating agent comprising the perfluoropolyether-modified silane as described in claim 1 or 2 and/or a partial hydrolytic condensate thereof as a main component.

Claim 4

An antireflection filter comprising an inorganic antireflection layer having a silicon dioxide-based inorganic layer as a surface layer and an antifouling layer formed on the surface layer, wherein the antifouling layer is given a sliding angle of oleic acid of 5° or less and a percent change of the sliding angle after solvent washing relative to the sliding angle before solvent washing of 10% or less.

Claim 5

The antireflection filter as described in claim 4, wherein the bonding force of the antifouling layer to an adhesive tape is 0.2 N/19 mm or less both before and after solvent washing.

Claim 6

The antireflection filter as described in claim 4 or 5, wherein the antifouling layer is formed from a perfluoropolyether-modified silane and/or a partial hydrolytic condensate thereof.

Claim 7

The antireflection filter as described in claim 6, wherein the perfluoropolyether-modified silane is represented by the following general formula (1):

[Chem. 2]



(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

Detailed Description of the Invention

[0001]

Industrial Field of Utilization

The present invention relates to a novel perfluoropolyether-modified silane having excellent water and oil repellency, parting properties, chemical resistance, lubricity, and the like, as well as excellent durability and antifouling properties, particularly fingerprint wipe-off, a surface treating agent including the same as a main component, and an antireflection filter including an antifouling layer having excellent antifouling properties and fingerprint wipe-off as well as particularly excellent durability.

[0002]

Prior Art

In general, perfluoropolyether-containing compounds have water and oil repellency, chemical resistance, lubricity, parting and antifouling properties, and the like because of their very low surface energy. For the effective utilization of such properties, these compounds are widely used in industry as water/oil repellent antifouling agents for paper, fibers, or the like, lubricants in magnetic recording media, oil repellents in precision machines, parting agents, cosmetic ingredients, protective coatings, or the like.

[0003]

The same properties, however, suggest that perfluoropolyether-containing compounds are non-tacky and non-adherent to other substrates. They have been applicable to these substrate surfaces, but it is difficult to form a film firmly bonded to the substrate.

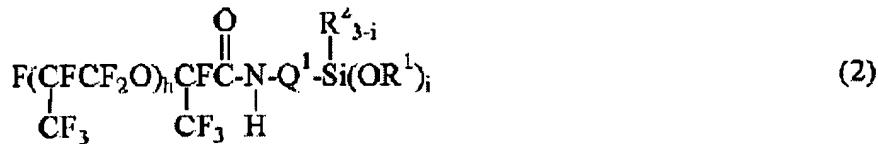
[0004]

On the other hand, silane coupling agents are well known as the means for establishing a firm bond between a substrate surface such as glass, fabric, and the like, and an organic compound. The silane coupling agent has an organic functional group and a reactive silyl group (generally an alkoxy silyl group) per molecule. The alkoxy silyl group undergoes a self-condensation reaction with airborne moisture, converting to a siloxane to form a film. At the same time, the silane coupling agent forms chemical and physical bonds with the surface of glass, metal, or the like, resulting in a durable tough film. By virtue of these properties, the silane coupling agent is widely used as a coating agent on the surfaces of a variety of substrates.

[0005]

As one exemplary compound which exhibits the above-mentioned characteristics, JP-A-58-167597 discloses a fluoroaminosilane compound represented by the following formula (2):

[Chem. 3]

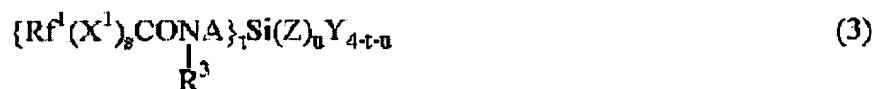


(wherein R¹ and R² are an alkyl group having 1 to 4 carbon atoms, Q¹ is CH₂CH₂CH₂ or CH₂CH₂NHCH₂CH₂CH₂, h is an integer of 1 to 4, and i is 2 or 3). These compounds, however, fail to fully take advantage of the perfluoropolyether group because the perfluoropolyether group portion is as short as consisting of two to five monomer units of hexafluoropropylene oxide (HFPO).

[0006]

Furthermore, JP-A-58-122979 discloses a compound represented by the following formula (3) as a water and oil repellent to be applied to a glass surface:

[Chem. 4]



(wherein Rf^d is a polyfluoroalkyl group having 1 to 20 carbon atoms, which may contain at least one ether bond, R³ is a hydrogen atom or a lower alkyl group, A is an alkylene group, X¹ is -CON(R⁴)-Q- or SO₂N(R⁴)-Q- (wherein R⁴ represents a lower alkyl group and Q represents a divalent organic group), Z represents a lower alkyl group, Y is halogen, an alkoxy group, or R⁵COO- (wherein R⁵ represents a hydrogen atom or a lower alkyl group), s represents an integer of 0 or 1, t represents an integer of 1 to 3, and u represents an integer of 0, or 1 to 2). However, these compounds do not exert fully satisfactory effects because the number of carbon atoms in the fluorinated group portion is as small as 1 to 20 carbon atoms.

[0007]

Particularly, since many tall buildings have been constructed recently, the demand for the technology for imparting "stain resistance" or "ease of stain removal" for keeping glazing maintenance-free is increasing, and for example, in order that display screens may be fingerprint-free for better outer appearance and visibility. There is a desire to develop a material meeting such demands.

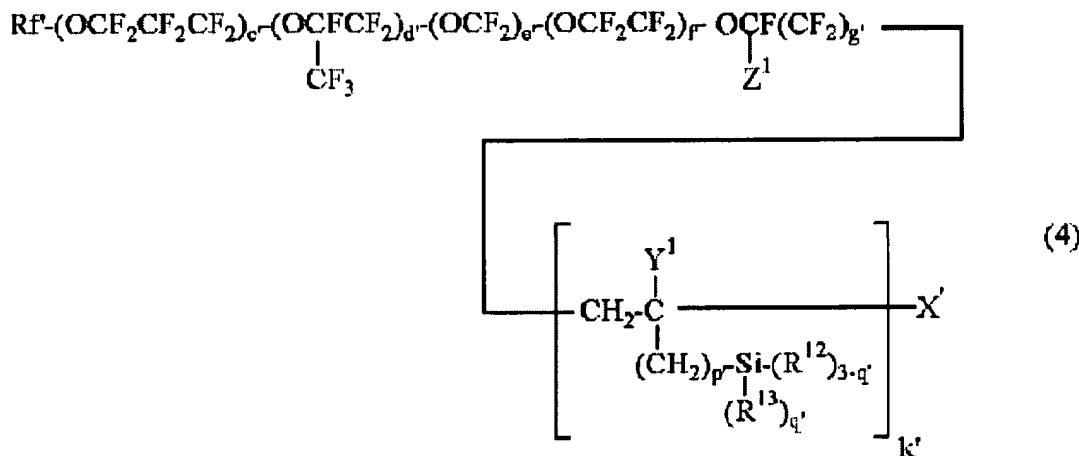
[0008]

There is known a lens, which uses a fluorine-containing silane compound of the following formula (4), as a surface treating agent, which can form a tough coating having excellent water and oil repellency, antifouling properties, chemical resistance,

lubricity, parting properties, and the like on the substrate surface by utilizing the above-described characteristics of a perfluoropolyether-containing compound and a silane coupling agent in an antifouling layer (JP-A-9-258003).

[0009]

[Chem. 5]



wherein Rf represents a straight chain or branched perfluoroalkyl group having 1 to 16 carbon atoms, X' represents iodine or hydrogen, Y^1 represents hydrogen or a lower alkyl group, Z^1 represents fluorine or a trifluoromethyl group, R^{12} represents a hydrolyzable group, R^{13} represents hydrogen or an inactive monovalent organic group, c , d , and f represent an integer of 0 to 200, g' represents 0 or 1, p and q' represent an integer of 0 to 2, and k' represents an integer of 1 to 10).

[0010]

However, the fluorine-containing silane compounds of the general formula (4) are insufficiently adhesive to substrates and unsatisfactorily durable because hydrolyzable groups are contained in a relatively large proportion, but only at one end of a molecule. Thus, when they are used as a surface treating agent for lenses, they fail to maintain the desired performance over a long term and are thus below the acceptable level in practical usage.

[0011]

Furthermore, antireflection films are generally provided on the surface of viewer equipment or the like. Such antireflection films tend to receive contaminants such as hand dirt, fingerprints, sweat, saliva, hair conditioners, and the like. When antireflection films are contaminated, surface reflectivity changes, or deposits are seen as white spots in relief to make display contents vague. There is the drawback that contaminants on the antireflection film become more obstructingly perceivable than on a simple transparent plate or the like. It has long been desired to have an

antireflection film which is excellent in preventing contaminants from being deposited thereon and allowing easy removal of contaminants which are deposited.

[0012]

Conventionally, there have been known antireflection films, having an antireflection layer including a single inorganic layer or plural inorganic layers having a surface layer including silicon dioxide formed by a PVD method as a main component, and a cured layer on the surface thereof of an organic polysiloxane-based polymer or a perfluoroalkyl group-containing polymer as an antireflection film which is intended to improve stain resistance or the like (JP-B-6-5324).

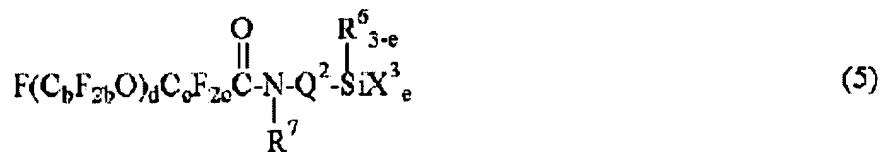
[0013]

However, when human contaminants such as hand dirt and fingerprints are deposited on this antireflection film, it is difficult to wipe off the contaminants with tissue paper or the like. The contaminants are extended and spread to a thin film when wiped, and the antireflection film can be marred on strong rubbing. Thus, there is a problem that there is no means of accomplishing satisfactory removal of the contaminants.

[0014]

Perfluoropolyether group-containing compounds generally have characteristics as mentioned above, and are thus utilized in the art. JP-A-11-29585 discloses an antireflection film, in which a perfluoropolyether-modified aminosilane represented by the following formula (5) is used in an antifouling layer. However, although this antireflection film has improved water and oil repellency, antifouling, chemical resistance, lubricity, parting properties, and the like, it has the problems of time-consuming curing and poor adhesion to substrates because polar groups having a high affinity to water, such as an amide group and the like, are contained in the molecule of perfluoropolyether-modified aminosilane used in the antifouling layer and the proportion (% by weight) of hydrolyzable groups per molecule is low. It has been required that the silane compound be given further sufficient performances before it can be used as a surface treating agent.

[Chem. 6]

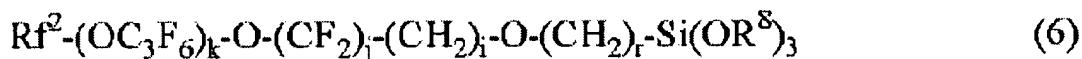


(wherein X^3 is a hydrolyzable group, R^6 is a lower alkyl group, R^7 is a hydrogen atom or lower alkyl group, Q^2 is $\text{CH}_2\text{CH}_2\text{CH}_2$ or $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2$, d is an integer of 6 to 50, e is 2 or 3, and b and c are each an integer of 1 to 3).

[0015]

In addition, JP-A-2001-188102 discloses an antireflection film, in which a perfluoropolyether group-containing silane coupling agent represented by the following formula (6) is used in an antifouling layer. The perfluoropolyether group-containing silane coupling agent used in the antifouling layer does not contain a polar group, but the proportion of hydrolyzable groups per molecule cannot be said to be fully high. Therefore, the perfluoropolyether group-containing silane coupling agent has problems of, for example, time-consuming curing and poor adhesion to a substrate, and thus, it cannot be said to have sufficient performance for being used as a surface treating agent.

[Chem. 7]



(wherein Rf^2 is a straight-chain or branched perfluoroalkyl group having 1 to 16 carbon atoms, R is an alkyl group having 1 to 10 carbon atoms, k is an integer of 1 to 50, r is an integer of 0 to 6, j is an integer of 0 to 3, i is an integer of 0 to 3, and $0 < j+i \leq 6$).

[0016]

Therefore, there is a desire to develop an antireflection filter which is less receptive to contaminants; which if the contaminants are deposited thereon, makes the contaminants less perceivable and makes it easy to wipe off the contaminants including human contaminants such as hand dirt, fingerprints, and the like with tissue paper or the like, and is resistant to marring by the wiping operation; which if water droplets or the like are deposited thereon, allows easy removal by shaking them off; and which retains for a long term the performances such as stain resistance, ease of wiping-off, mar resistance, water repellency, and the like.

[0017]

- [Patent Document 1] JP-A-58-167597
- [Patent Document 2] JP-A-58-122979
- [Patent Document 3] JP-A-9-258003
- [Patent Document 4] JP-B-6-5324
- [Patent Document 5] JP-A-11-29585
- [Patent Document 6] JP-A-2001-188102

[0018]

Problems to Be Solved by the Invention

Therefore, the present invention has been made to meet the above-described demands, and has an object to provide a novel perfluoropolyether-modified silane having excellent water and oil repellency, parting properties, chemical resistance, lubricity, and the like, as well as excellent durability and antifouling properties,

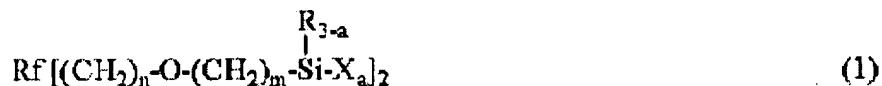
particularly fingerprint wipe-off, a surface treating agent including the same as a main component, and an antireflection filter including an antifouling layer having excellent antifouling properties and fingerprint wipe-off as well as particularly excellent durability.

[0019]

Means to Solve Problems

The present inventors have investigated extensively to meet the above-described demands and as a result, they have discovered that a perfluoropolyether-modified silane having the following general formula (1) has excellent water and oil repellency, parting properties, chemical resistance, lubricity, durability, and antifouling properties, and particularly excellent fingerprint wipe-off, can be used as a surface treating agent, and is suited to form a cured film on the surface of an antireflection filter, thereby leading to completion of the present invention.

[Chem. 8]



(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

[0020]

The present inventors have also found that by forming an antifouling layer on a surface layer of an inorganic antireflection layer having a silicon dioxide-based inorganic layer, in which the antifouling layer is given a sliding angle of oleic acid of 5° or less as by forming the layer from the silane of the formula (1), and the percent change of the sliding angle after solvent washing relative to the sliding angle before solvent washing is controlled to 10% or less, an antireflection filter, wherein the antifouling layer has a low surface energy and a minimized sticking force for contaminants, retains such effects for a long term, is resistant to deposition of contaminants such as fingerprints, skin grease, sweat, cosmetics, and the like, even if contaminants are deposited thereon, the antifouling layer makes it easy to wipe off the contaminants and experiences a minimal reduction in its function by rubbing, the antireflection layer receives fewer mars on its surface, and the separation of the antireflection layer promoted by mars can be prevented, can be obtained, thereby leading to completion of the present invention.

[0021]

Accordingly, the present invention provides a perfluoropolyether-modified silane having the general formula (1). Further, the present invention provides a surface treating agent including the perfluoropolyether-modified silane and/or a

partial hydrolytic condensate thereof as a main component. Also, the present invention provides an antireflection filter, including an inorganic antireflection layer having a silicon dioxide-based inorganic layer as a surface layer and an antifouling layer formed on the surface layer, wherein the antifouling layer is given a sliding angle of oleic acid of 5° or less and a percent change of the sliding angle after solvent washing relative to the sliding angle before solvent washing of 10% or less, particularly an antifouling layer formed of the perfluoropolyether-modified silane of the formula (1) and/or a partial hydrolytic condensate thereof.

[0022]

Hereinbelow, the present invention will be described in more detail. The perfluoropolyether-modified silane of the present invention is represented by the following general formula (1).

[0023]

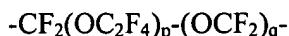
[Chem. 9]



(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

[0024]

Herein, Rf is a divalent straight-chain perfluoropolyether group, and includes perfluoropolyether groups of differing chain length, and preferably a divalent straight-chain perfluoropolyether group containing recurring units of a perfluoropolyether having about 1 to 4 carbon atoms. Examples of the divalent straight-chain perfluoropolyether group include those shown below.



In the above chemical structural formulae, k, p, and q are each an integer of at least 1, specifically, in the range of 1 to 50, and more preferably in the range of 10 to 40. Further, the molecular structure of the perfluoropolyether is not limited to these exemplified structures.

[0025]

X represents a hydrolyzable group. Specific examples thereof include alkoxy groups such as a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like, alkoxyalkoxy groups such as a methoxymethoxy group, a methoxyethoxy group, and the like, acyloxy groups such as an acetoxy group and the like, alkenyloxy groups such as an isopropenoxy group and the like, halogen groups such as a chloro group, a bromo group, an iodo group, and the like; etc. Of these,

organooxy groups such as an alkoxy group, an alkenyloxy group, and the like, and a chloro group are preferred, and a methoxy group, an ethoxy group, an isopropenoxy group, and a chloro group are further preferred.

[0026]

R is a lower alkyl group of 1 to 4 carbon atoms or a phenyl group, and specific examples thereof include a methyl group, an ethyl group, a phenyl group, and the like, among which a methyl group is preferred. n is an integer of 0 to 2, and preferably 1. Further, m is an integer of 1 to 5, and preferably 3. a is 2 or 3, and preferably 3 from the standpoints of reactivity and adhesion to the substrate.

[0027]

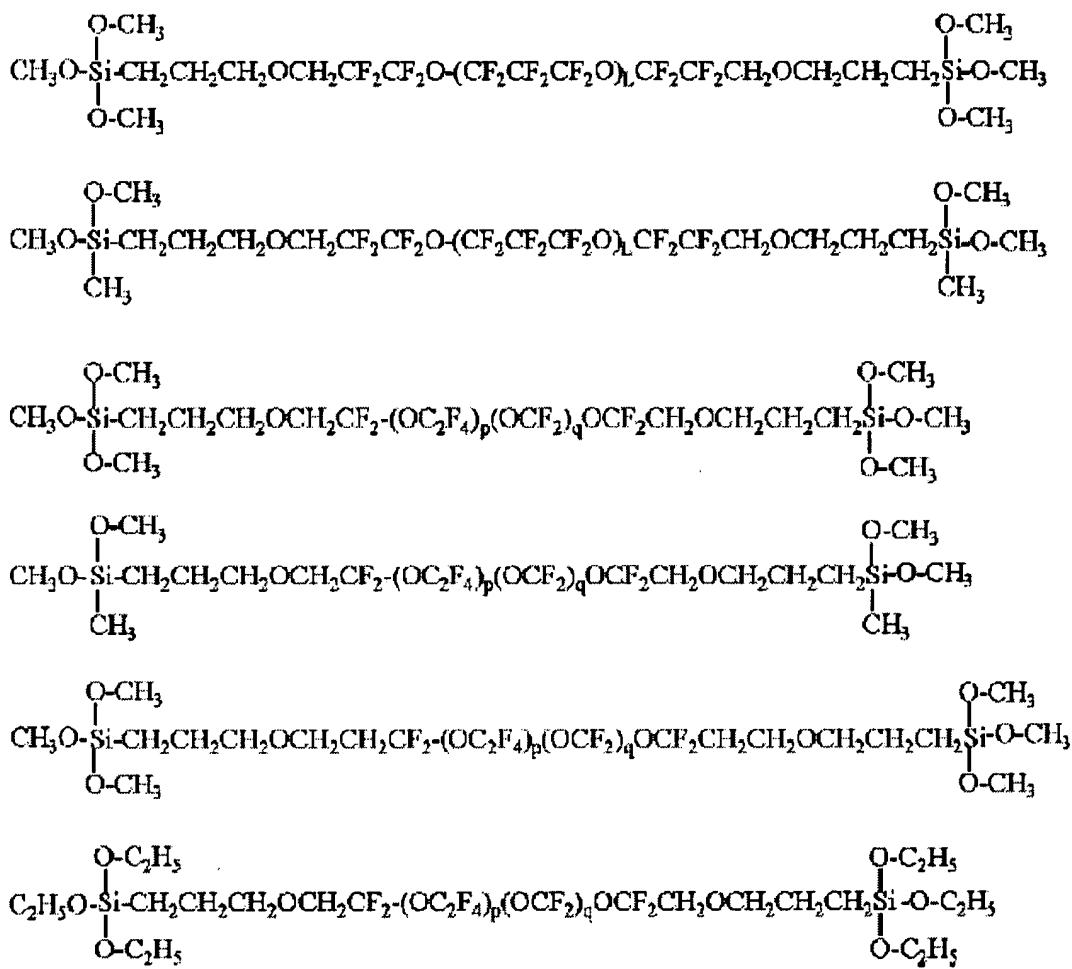
The molecular weight of the perfluoropolyether-modified silane compound of the present invention is not particularly limited, but the number average molecular weights of 500 to 20000, and preferably 1000 to 10000 are appropriate from the standpoints of stability, ease of handling, and the like.

[0028]

Specific examples of the perfluoropolyether-modified silanes include those represented by the following structural formulae, but are not limited to the examples below.

[0029]

[Chem. 10]



(wherein L is an integer of 1 to 50, p is an integer of 1 to 50, q is an integer of 1 to 50, a sum of p+q is an integer of 10 to 100, and the arrangement of recurring units is random). These may be used singly or in combination of two or more kinds thereof.

[0030]

Examples of the method for preparing the perfluoropolyether-modified silane of the present invention include a method in which a hydrosilane having a hydrolyzable group is added to a perfluoropolyether containing an α -unsaturated bond at both ends in the presence of a platinum-based catalyst according to a conventional hydrosilylation procedure.

[0031]

[Chem. 11]



(wherein Rf, R, X, n, m, and a are as defined above).

[0032]

Herein, as a method for synthesizing a perfluoropolyether containing α -unsaturated bonds at both ends, there is a method in which the perfluoropolyether is obtained by reacting a both end alcohol-modified perfluoropolyether represented by the following formula (7) with an alkali metal such as K, Na, Li, and the like or an alkali metal hydroxide such as KOH, NaOH, LiOH, and the like to produce a both end alcoholate-modified perfluoropolyether represented by the formula (8) and reacting it with an α -unsaturated bond-containing halide.



(wherein n is as defined above and M is an alkali metal).

[0033]

Since the perfluoropolyether-modified silane of the present invention does not contain in its molecule a polar group which can be detrimental to the properties of the silane, it is excellent in terms of water and oil repellency, antifouling properties, chemical resistance, lubricity, parting properties, and the like, and the silane can thus be used as a surface treating agent by coating it to the surfaces of various substrates. Since at least two hydrolyzable groups such as a hydrolyzable silyl group and the like are located at both ends of its molecule, the silane at both ends is firmly bound to the substrate so that its effect can last for a long time.

[0034]

Examples of utilities of the above function include those shown below:

Water and oil repellents	for paper, fabric, metals, glass, plastics, ceramics, or the like,
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Parting agents	for adhesive tapes, resin molding molds, rolls, or the like,
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Antifouling processing agents	for paper, fabric, metals, glass, plastics, ceramics, or the like, and
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Other agents	for paint additives, resin modifiers, agents for modifying the flowability and dispersibility of inorganic fillers, and agents for improving the lubricity of tapes, films, and the like, etc.
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[0035]

The perfluoropolyether-modified silane of the present invention is preferably used as a surface treating agent, and can be used to form a cured film on the surface of an antireflection filter. The surface treating agent of the present invention includes the perfluoropolyether-modified silane represented by the formula (1) and/or a partial hydrolytic condensate thereof as a main component.

[0036]

If necessary, an organooxysilane hydrolytic condensation catalyst may be added to the surface treating agent. Examples of the organooxysilane hydrolytic condensation catalyst include organic tin compounds such as dibutyltin dimethoxide, dibutyltin dilaurate, and the like, organic titanium compounds such as tetra-n-butyl titanate, and the like, organic acids such as acetic acid, methanesulfonic acid, and the like, and mineral acids such as hydrochloric acid, sulfuric acid, and the like. Particularly, acetic acid, tetra-n-butyl titanate, dibutyltin dilaurate, and the like are preferable. The addition amount thereof is a usual catalytic amount, and it is preferably 0.01 to 5 parts by weight, and particularly preferably 0.1 to 1 part by weight, based on 100 parts by weight of the perfluoropolyether-modified silane and/or a partial hydrolytic condensate thereof.

[0037]

Furthermore, for the treating agent of the present invention, the perfluoropolyether-modified silane and/or a partial hydrolytic condensate thereof may be used as such or diluted with a suitable solvent. The solvent may be a mixture of two or more solvents, and it is preferable to dissolve uniformly the perfluoropolyether-modified silane and/or a partial hydrolytic condensate thereof therein.

[0038]

Examples of the solvent include fluorine-modified aliphatic hydrocarbon-based solvents such as perfluoroheptane, perfluoroctane, and the like, fluorine-modified aromatic hydrocarbon-based solvents such as m-xylene hexafluoride, benzotrifluoride, and the like, fluorine-modified ether-based solvents such as methylperfluorobutyl ether, perfluoro(2-butyltetrahydrofuran), and the like, fluorine-modified alkylamine-based solvents such as perfluorotributylamine, perfluorotripentylamine, and the like, hydrocarbon-based solvents such as petroleum benzine, mineral spirits, toluene, xylene, and the like, and ketone-based solvents such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like. Of these, the fluorine-modified solvents are preferable from the standpoints of solubility, wetting properties, and the like, and in particular, m-xylene hexafluoride, perfluoro(2-butyltetrahydrofuran), perfluorotributylamine, and the like are preferable.

[0039]

For a method for forming a film, the treatment can be carried out by well-known methods such as brush coating, dipping, spraying, vapor deposition treatment, and the like. The optimal treatment temperature varies depending on the treating methods, and for example, in the case of brush coating or dipping, the temperature is preferably in the range from room temperature to 120°C. For the treatment humidity, the treatment is preferably carried out under humidified conditions for promotion of the reaction, but it is preferable that the treatment humidity be optimized on every application with additives depending on a particular silane compound and other additives used.

[0040]

As a substrate on which a film is formed, substrates made of various materials such as paper, fabric, metals, metal oxides, glass, plastics, porcelain, ceramics, or the like can be used.

[0041]

Herein, examples of the articles having a cured film formed on their surfaces include optical members such as eyeglass lenses, antireflection filters, and the like (coatings for preventing fingerprint and grease contamination), sanitary ware such as bathtubs and washbowls (water repellent, antifouling coatings), glazing and head lamp covers in vehicles such as automobiles, trains, aircraft, and the like (antifouling coatings), building exteriors (water repellent, antifouling coatings), kitchen ware (coatings for preventing oil contamination), telephone booths (water repellent, antifouling, anti-sticking coatings), artistic objects (water and oil repellent, anti-fingerprint coatings), compact discs and DVDs (coating for preventing fingerprint), and the like. The surface treating agent of the present invention is particularly suited to form a film on optical members such as a lens, a filter, and the like to impart antireflection properties, antifouling properties, and the like thereto.

[0042]

The present invention further provides an antireflection filter, and particularly an antireflection filter having on its surface a cured film of the perfluoropolyether-modified silane represented by the formula (1) and/or a partial hydrolytic condensate thereof. The antireflection filter includes an antireflection layer having a silicon dioxide-based inorganic layer as a surface layer, and an antifouling layer formed on the surface layer, wherein the antifouling layer is given a sliding angle of oleic acid of 5° or less, and a percent change of the sliding angle after solvent washing relative to the sliding angle before solvent washing of 10% or less.

[0043]

Herein, the antifouling layer has a sliding angle of oleic acid of 5° or less, preferably 3° or less. A percent change of the sliding angle after solvent washing relative to the sliding angle before solvent washing is 10% or less, preferably 5% or

less. If the sliding angle of oleic acid is more than 5°, the layer has poor antifouling properties so that it is readily marked with fingerprints or the like, and it becomes difficult to wipe off contaminants and less slippery on the surface during the wiping in some cases.

[0044]

If the percent change of the sliding angle B after solvent washing relative to the sliding angle A before solvent washing $[(B-A)/A] \times 100$ is more than 10%, then antifouling and fingerprint wipe-off properties may not last for a long time in some cases. Further, the sliding angle of oleic acid is measured using a conventional contact angle meter. Solvent washing is carried out by immersing a sample in the solvent for 5 minutes, taking out the sample and allowing the solvent to lightly flow away. The solvent may be one used in conventional washing, for example, HCFC-225, nonafluorobutyl methyl ether, and the like.

[0045]

Also, the bonding force of the antifouling layer to adhesive tape is preferably 0.2 N/19 mm or less both before and after solvent washing. If the bonding force of the antifouling layer to adhesive tape is more than 0.2 N/19 mm, then fingerprint wipe-off properties may be insufficient in some cases. The bonding force of the antifouling layer to adhesive tape is measured by attaching a polyester adhesive tape to the surface of the antifouling layer and pulling the tape at an angle of 180° and a peeling rate of 300 mm/min by means of a tensile tester.

[0046]

In this case, the antifouling layer is preferably formed of a perfluoropolyether-modified silane, and particularly preferably formed as a cured film of the perfluoropolyether-modified silane represented by the following general formula (1) or a partial hydrolytic condensate thereof.

[Chem. 12]



(wherein Rf is a divalent straight-chain perfluoropolyether group, R is an alkyl group or phenyl group having 1 to 4 carbon atoms, X is a hydrolyzable group, n is an integer of 0 to 2, m is an integer of 1 to 5, and a is 2 or 3).

[0047]

Examples of the method for forming the antifouling layer include well-known methods such as brush coating, dipping, spraying, vapor deposition treatment, and the like. The optimal treatment temperature varies depending on the treating methods, and for example, in the case of brush coating or dipping, the temperature is preferably in the range from room temperature to 120°C. For the treatment humidity, the

treatment is preferably carried out under the humidified conditions for promotion of the reaction, but it is preferable that the treatment humidity be optimized on every application with additives depending on a particular silane compound and other additives used.

[0048]

In such a coating operation, the perfluoropolyether-modified silane may be used as such or diluted with a suitable solvent. The solvent may be a mixture of two or more solvents, and it is preferable to dissolve uniformly the perfluoropolyether-modified silane therein.

[0049]

As a solvent, the same as described above can be used. If necessary, an organooxysilane hydrolytic condensation catalyst as described above may be added thereto.

[0050]

Further, the film thickness of the antifouling layer is properly determined, but it is preferably usually in the range from 0.1 nm to 5 µm, and particularly from 1 to 100 nm.

[0051]

The antireflection filter of the present invention is an antireflection filter, including an inorganic antireflection layer having a silicon dioxide-based inorganic layer as a surface layer, and an antifouling layer formed on the surface layer. The inorganic antireflection layer is preferably provided on a supporting substrate directly or through an intermediate layer such as a hard coat layer and the like. FIGS. 1 and 2 illustrate these antireflection filters, in which 1 is a supporting substrate, 2 is an intermediate layer, 3 is an inorganic antireflection layer, and 4 is an antifouling layer.

[0052]

Herein, the inorganic antireflection layer is a portion that contributes to a substantial antireflection function, and in the present invention, it may have a suitable structure of either a single layer structure or a plural layer structure, but the surface layer of the antireflection film is preferably a silicon dioxide-based inorganic layer.

[0053]

Accordingly, the inorganic antireflection layer may be formed as an antireflection layer of a structure according to a conventional art, as described, for example, in JP-A-58-46301, JP-A-59-49501, JP-A-58-50401, JP-A-1-294709, JP-B-6-5324, and the like.

[0054]

It is preferable from the standpoint of antireflection effects that the antireflection layer have a plural layer structure. Particularly preferred is a plural layer structure including a silicon dioxide-based inorganic layer as a surface layer and

one or more layers having a higher index of refraction than the silicon dioxide-based inorganic layer. In this case, the thickness, the index of refraction, and the like of the respective layers are determined according to the well-known technology.

[0055]

In forming the inorganic antireflection layer, inorganic materials such as inorganic oxides, inorganic halides, composites thereof, and the like can be used. Specific examples of the inorganic materials include inorganic oxides such as SiO₂, ZrO₂, Al₂O₃, Y₂O₃, TiO₂, and the like, and inorganic halides such as MgF₂, BaF₂, CaF₂, LaF₂, LiF, NaF, SrF₂, and the like.

[0056]

As the inorganic materials which form the antireflection layer, one or more inorganic materials may be used in any suitable form such as a solid form, a dispersion form, and the like in a binder polymer or the like, depending on a particular forming method to be described below. In this case, from the standpoints of hardness and stain resistance, it is preferable to use a composition containing at least 30% by weight of inorganic materials. Further, any suitable polymer may be used as a polymer for the binder and is not particularly limited. However, various organosilicon compounds capable of forming polyorganosiloxanes and hydrolyzates thereof, and the like are preferred from the standpoints of hardness or the like.

[0057]

Formation of the inorganic antireflection layer may be carried out by suitable thin-film forming methods, for example, various PVD (Physical Vapor Deposition) methods such as typically a vacuum deposition method, a sputtering method, an ion plating method, and the like, or fluid applying methods such as typically a spin coating method, a dip coating method, a curtain flow coating method, a roll coating method, a spray coating method, a flow casting method, and the like, and other methods.

[0058]

For the PVD methods, inorganic oxides such as SiO₂ and the like and inorganic halides such as MgF₂ and the like as exemplified above are preferably used. From the standpoints of the level of surface hardness and adhesion to the antifouling layer, it is particularly preferable that the silicon dioxide-based inorganic layer serving as the surface layer be formed by the PVD method as a layer containing silicon dioxide as a main component.

[0059]

Furthermore, in the inorganic antireflection layer, a conductive layer may be included that exerts the effect of removing static electricity for preventing dust and debris from being deposited under the impetus of static build-up and the effect of shielding electromagnetic waves. Such a conductive layer is typically formed as a

metal thin film of gold, silver, aluminum, and the like or a transparent conductive film in the form of an inorganic oxide thin film of tin oxide, indium oxide, a mixture thereof (ITO), and the like. Most preferred are transparent conductive films based on inorganic oxides which show minimized absorption of light in the visible region.

[0060]

On the other hand, a supporting substrate used herein may be any suitable one and is not particularly limited. However, the supporting substrates of glass and plastics are preferred when the antireflection film is formed by a liquid coating method or the like. Further, an antireflection filter in which the inorganic antireflection layer 3 is provided on one side of the supporting substrate 1 is illustrated in the figure, but the inorganic antireflection layer 3 may be provided either on one side or on both sides of the supporting substrate 1.

[0061]

When the supporting substrate is glass, a low refractive index material such as MgF₂, CaF₂, and the like is preferably incorporated in the antireflection layer, for example, from the standpoint that a better reflection effect is achievable. Further, in the case of a plastic substrate, a material having a relatively low refractive index and a high hardness such as SiO₂ is preferably incorporated in the antireflection layer from the standpoints of durability and the like. Examples of the material for the plastics include acrylic resins, diethylene glycol bisallyl carbonate resins, polycarbonate-based resins, polyester-based resins such as polyethylene terephthalate, unsaturated polyesters, and the like, acetate-based resins such as triacetyl cellulose, styrene resins, polyvinyl chloride resins, and the like, and others.

[0062]

The supporting substrate may have any suitable shape such as a film, a sheet, a plate, and the like while its thickness is not arbitrary. The supporting substrate may have a hard coat layer thereon as the intermediate layer. In this case, the antireflection filter is structured such that the hard coat layer 2 is disposed between the antireflection layer 3 and the supporting substrate 1 as shown in FIG. 2.

[0063]

The hard coat layer may be formed in a conventional manner. Preferred is a hard coat layer which is formed of a cured product of an organosilicon compound, particularly an organosilicon compound represented by the following general formula (9), or a hydrolyzate thereof.



(wherein R⁹ and R¹⁰ are an alkyl group, an alkenyl group, an aryl group, or a hydrocarbon group having a halogen group, an epoxy group, a glycidoxyl group, an amino group, a mercapto group, a methacryloxy group, a cyano group, or the like, R¹¹

is an alkyl group having 1 to 8 carbon atoms, an alkoxyalkyl group, an acyl group, an aryl group, or the like. f and g are 0 or 1 and f+g is 0, 1, or 2).

[0064]

The hard coat layer may be provided as a layer having an anti-glare function by a suitable method, for example, a method of including small particles of silica or metal oxide having an average particle size of 0.5 to 5 μm using a sol-gel process or the like; or a method of roughening the surface to a centerline average roughness of 0.01 to 0.5 μm by buffering, corona discharge treatment or ion etching.

[0065]

Furthermore, instead of or along with the hard coat layer, the supporting substrate may have a suitable coat layer or be surface treated for the purposes of enhancing adhesion of the antireflection film, hardness, chemical resistance, durability, dyeability, or the like as the intermediate layer.

[0066]

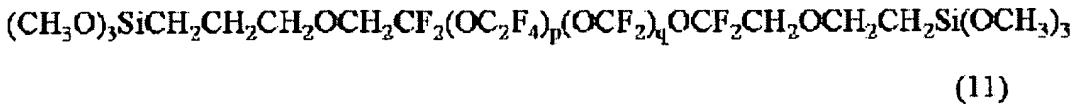
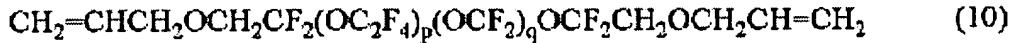
Moreover, for the purposes of enhancing the hardness, suitable hardening materials may be used as described, for example, in JP-B-50-28092, JP-B-50-28446, JP-B-50-39449, JP-B-51-24368, JP-B-57-2735, JP-A-52-112698, and the like. In addition, a method of coating an oxide of a metal such as titanium, aluminum, tin, and the like or an oxide of silicon and the provision of an acrylic crosslinked material such as (meth)acrylic acid crosslinked with pentaerythritol, etc. and the like, etc. are also effective for enhancing the hardness

[0067]

[Examples] Synthesis Example, Examples and Comparative Examples are given below to specifically illustrate the present invention. The present invention is not limited to the Examples. All parts are by weight.

[0068] [Synthesis Example] To a mixture of 160 g of a perfluoropolyether having an α -unsaturated bond at both ends represented by the following formula (10), 80 g of m-xylene hexafluoride, and 0.1 g of a catalyst of chloroplatinic acid modified with $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$ was added dropwise 15 g of trimethoxysilane in a dry air atmosphere at 70°C. The contents were stirred for 8 hours for reaction, and then the solvent was distilled off, to yield 165 g of a colorless clear liquid (viscosity 45.5 cSt, specific gravity 1.730, refractive index 1.305) represented by the following formula (11).

[Chem. 13]



$$p/q \approx 0.9 \quad p+q \approx 4.5$$

[0069] [Example 1] An ethanol solution primarily containing 135 parts by weight of silica sol, 129 parts by weight of γ -glycidoxy-propyltriethoxysilane in a hydrolyzate form and 70 parts by weight of γ -chloropropyltrimethoxysilane in a hydrolyzate form was applied to a PET film (100 μm thick) and cured to form a hard coat layer 3 μm thick. On the hard coat layer, five layers of SiO_2 layer, TiO_2 layer, SiO_2 layer, TiO_2 layer, and SiO_2 layer were alternately deposited each to a $\lambda/4$ optical film thickness by a sputtering method to provide an antireflection layer. Next, a coating solution was prepared by dissolving 0.2 g of the compound 1 represented by the formula (11) obtained in Synthesis Example in 99.8 g of perfluoro(2-butyltetrahydrofuran). This treatment liquid was applied onto the antireflection layer by a spin coating method. The coating was allowed to stand for 24 hours in an atmosphere of 25°C and a humidity of 70%, and then cured to form an antifouling layer. The sample thus obtained was examined by the following tests (1) to (3). The results are shown in Table 1.

[0070]

(1) Evaluation of Surface Properties

(i) Sliding Angle

Using a contact angle meter (Model CA-A prepared by Kyowa Interface Science Co., Ltd.), the sliding angle of a 2-mm diameter droplet of oleic acid on the antifouling layer was measured. Measurement was made at five different points on the surface, and an average was reported.

(ii) Bonding Force

A polyester adhesive tape (No. 31B prepared by Nitto Denko Co., Ltd., 19 mm wide) was attached to the surface of the antifouling layer. By using a tensile tester and pulling the tape at an angle of 180° and a peeling rate of 300 mm/min, the force required to peel the adhesive tape was measured.

(2) Evaluation of Durability of Film

The sample was immersed for 5 minutes in a fluorinated solvent (AK-225 prepared by Asahi Glass Co., Ltd.), taken out, and dried. Then, the sliding angle and the bonding force were measured by the same tests (i) and (ii) to evaluate durability

(3) Evaluation of Antifouling Properties

A forefinger was pressed against the surface of the antifouling layer for 5 seconds to mark a fingerprint. Then, the fingerprint was wiped with dry fabric to evaluate the ease of fingerprint wipe-off. Evaluation was made according to the following criteria and reported as an average of five panel members.

Ease of Fingerprint Wiping-Off

O: Light wiping of fingerprint

Δ: Difficult to wipe off fingerprint, but no track

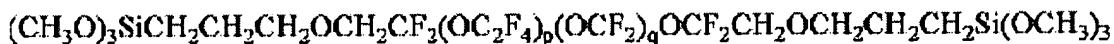
×: Difficult to wipe off fingerprint with track left

[0071] [Comparative Examples 1 to 3] The samples were evaluated by the same method as in Example except that Compounds 2 to 4 shown below were used instead of perfluoropolyether-modified silane of Compound 1. The evaluation results are shown in Table 1.

[0072]

[Chem. 14]

Compound 1

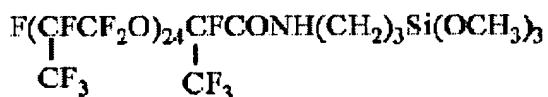


$$p/q \approx 0.9 \quad p+q \approx 4.5$$

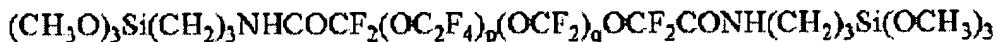
Compound 2



Compound 3



Compound 4



$$p/q \approx 0.6 \quad p+q \approx 6.0$$

[0073]

[Table 1]

	Sliding angle (deg)		Bonding force (N/19 mm)		Fingerprint wipe-off
	Before washing	After washing	Before washing	After washing	

Example	Compound 1	1.8	1.8	0.12	0.14	O
Comparative Example	Compound 2	2.5	11.3	0.10	0.37	O
	Compound 3	3.4	10.4	0.19	0.37	Δ
	Compound 4	6.2	6.5	0.29	0.34	Δ

[0074]

The Example has superior surface properties compared with the Comparative Examples, and further, is excellent in terms of durability and fingerprint wipe-off.

[0075]

[Effect of the Invention] Since the perfluoropolyether-modified silane in the present invention does not contain in its molecule a polar group which can be detrimental to the properties, it is excellent in terms of water and oil repellency, parting properties, chemical resistance, lubricity, durability, antifouling properties, and fingerprint wipe-off, and the silane can thus be used as a surface treating agent for coating on the surfaces of various substrates and is applicable to an antireflection filter by forming a cured film thereon a surface. Further, the antireflection filter is resistant to staining, allows easy wiping off of such stains, and has good surface lubricity and resistance to marring, and maintains such properties over a long term. The antireflection filter can be used in various optical elements such as viewers on an LCD and the like, polarizers, and the like.

[0076]

Brief Description of the Drawings

Fig. 1

FIG. 1 is a cross-sectional view showing an example of the antireflection filter according to the present invention.

Fig. 2

FIG. 2 is a cross-sectional view showing another example of the antireflection filter according to the present invention.

Description of Symbols

- 1 SUPPORTING SUBSTRATE
- 2 INTERMEDIATE LAYER
- 3 INORGANIC ANTIREFLECTION LAYER
- 4 ANTIFOULING LAYER